

ARMY RESEARCH LABORATORY



An Initial Study of the Atmospheric Fate of Iodine From Halon Alternatives

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13. ABSTRACT (Maximum 200 words) One class of compounds being considered as replacements for the presently used Halons are iodinated fluorocarbons. This report addresses some of the outstanding questions regarding the atmospheric chemistry of these proposed alternative compounds and their by-products from either intentional or accidental release. Very little information on the atmospheric chemistry of iodinated compounds is known, thus this work fills a timely and pressing need to answer questions, such as, what are the ozone depletion potential (ODP) and global warming potential (GWP) of such compounds?				
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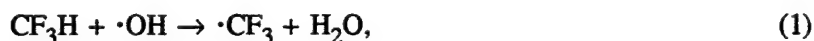
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1. INTRODUCTION

There is a continuing and urgent need to establish the environmental acceptability and impact of new, military-specific candidate replacements for Halons and other ozone depleting compounds. This includes determining the atmospheric lifetimes, ozone depletion potential (ODP), global warming potential (GWP), and possible atmospheric production of toxic compounds. The recent requirements for the cessation of the sale and use of ozone depleting chemicals has created a new concern for the environmental impact of the use of replacement compounds. By design, most of these new replacement compounds have a much shorter atmospheric lifetime than the ozone depleting compounds. However, the products of their initial, or subsequent, atmospheric reactions may themselves be significant global warming gases. Specifically, this is the case if the parent compounds are highly fluorinated. These products of atmospheric reactions may also be quite toxic, and thus may present a threat to the ecosystem. Not surprisingly, relatively little research has been done so far to ascertain the impact on the lower atmosphere as a result of the use of replacement compounds because the transition to these replacement compounds is only now beginning. This report deals with two specific aspects of the atmospheric fate of certain candidate Halon replacement compounds. The first involves the study of reactivity of haloperoxy radicals, while the second involves the determination of the absorption cross sections for one of the leading Halon replacement candidate compounds, CF_3I .

2. REACTIONS OF PERHALOALKYLPEROXYL RADICALS

Most of the chemical compounds under consideration as possible replacements for the Halons and chlorofluorocarbons (CFCs) are expected to degrade in the atmosphere, either because they contain one or more C-H bonds which are subject to attack by atmospheric hydroxyl radicals, for example,



or because they may be photodissociated in the atmosphere, for example,



The resulting carbon-centered radical will rapidly react with oxygen to produce a halogenated peroxy radical



Subsequent reactions of the peroxy radical lead to the removal of the halogens from the atmosphere. There is, presently, a limited amount of information on the possible atmospheric reactions of these halogenated peroxy radicals. Peroxy radicals generally are expected to react with NO, NO₂, or with other peroxy radicals, including HO₂· (Wallington et al. 1992). Other reactions of peroxy radicals (e.g., with alkenes) generally are considered to be too slow to be of any importance in the atmosphere. Whereas this is clearly true for the nonhalogenated alkylperoxy radicals, halogenation may increase the reactivity of these radicals sufficiently so that other reaction pathways become important.

Formation and reactions of halogenated peroxy radicals might also relate to potential physiological effects of these halocarbon replacements. For example, the toxicity of CCl₄ has been suggested to arise from reactions of CCl₃O₂·, formed after the one-electron reduction of the parent. These peroxy radicals are strong oxidants and will react with antioxidants, such as vitamin C or vitamin E, but also may react with other physiological molecules, such as lipids, initiating damage (Slater 1978; Recknagel and Glende 1973; Brault 1985; Neta, Huie, and Ross 1990).

3. EXPERIMENTAL SECTION*

The rate constants for reactions of perhaloalkylperoxy radicals with the various alkenes in methanolic solutions were determined by pulse radiolysis. Air-saturated stock solutions containing 0.5–2% halocarbon and $1 \times 10^{-4} - 5 \times 10^{-3} \text{ mol L}^{-1}$ chlorpromazine were prepared for the liquid halocarbons. For the gaseous halocarbons, mixtures were prepared by adding a halocarbon-saturated chlorpromazine solution to oxygen-saturated methanol. A fresh sample of the solution was introduced into the irradiation cell with a syringe and was irradiated under aerobic conditions with a single pulse of 2-MeV electrons, with a dose of about 10 Gy.

The irradiation of methanol by ionizing radiation results in the formation of solvated electrons, radical cations, methoxy radicals, and hydrogen atoms (Getoff et al. 1993; Dainton et al. 1969; Johnson and Salmon 1977).

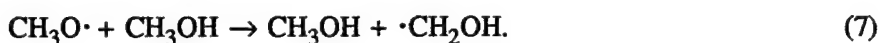
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The radical cation will deprotonate,



The hydrogen atom and the methoxyl radical will react with the solvent to produce the hydroxymethyl radical, with $k_6 = 2.6 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ and $k_7 = 2.6 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$



Halogenated alkyl radicals are produced by the reduction of chlorine-, bromine-, or iodine-containing halocarbons by the solvated electron, for example:



In the presence of oxygen, haloalkylperoxyl radicals are formed rapidly, $k_9 \sim 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ (Neta et al. 1990).



Although $\cdot\text{CH}_2\text{OH}$ is a reducing radical, it does not react rapidly with the haloalkenes used in this study and should react with oxygen to make the alkylperoxyl radical $\text{HOCH}_2\text{O}_2^\cdot$. This radical has much lower reactivity than the haloalkylperoxyl radicals under investigation here and, therefore, does not interfere with these kinetic measurements (Neta et al. 1990).

In our pulse-radiolysis apparatus, reactions are monitored by kinetic spectrophotometry. Peroxyl radicals absorb only in the ultraviolet, primarily below 280 nm, and this absorption is not particularly strong. The same is true of any expected products of the reaction of these radicals with alkenes. With our apparatus, measurements are difficult in this spectral region, so, rather than following the reaction directly, we have determined the rate constants by competition kinetics using chlorpromazine (ClPz) as

a reference. The rate of oxidation of ClPz is determined directly by following the formation of the ClPz radical at 525 nm.



The addition of alkenes to solutions of ClPz leads to competition between reaction 10 and 11.



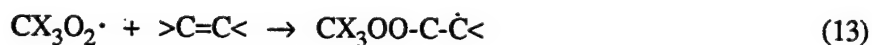
This will result in an enhanced rate of formation and decreased yield of $\text{ClPz}^\cdot{}^+$. At constant ClPz concentration, the observed rate of formation of $\text{ClPz}^\cdot{}^+$ (k_{obs}) is given by:

$$k_{obs} = k_0 + k_1[\text{alkene}], \quad (12)$$

where k_0 is the first-order rate constant in the absence of alkene, which includes the rate of reaction 10 and any other loss processes for the peroxy radical except reaction 11, and k_1 is the second-order rate constant for reaction 11. The second-order rate constant is derived from the slope of a plot of the first-order rate constant against alkene concentration. At least three separate experiments were performed for each alkene concentration, and at least three alkene concentrations were employed for each alkene-radical reaction.

4. RESULTS AND DISCUSSION

4.1 Effect of Alkene Substituents on the Addition Reaction. The rate constants for the reactions of $\text{CF}_3\text{CCl}_2\text{O}_2^\cdot$ with 10 alkenes (Table 1) vary between 5×10^4 and $3 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$. The variation in rate constant with substituents about the double bond is consistent with addition as the main reaction path.



The same pattern was observed for the reactions of other halogenated peroxy radicals (Nahor and Neta 1991; Alfassi, Huie, and Neta 1993). The results for $\text{CCl}_3\text{O}_2^\cdot$ and $\text{CBr}_3\text{O}_2^\cdot$ are included in Table 1 for comparison. The conclusion that the primary reaction is electrophilic addition is based on the good

Table 1. Rate Constants for Reactions of $\text{CF}_3\text{CCl}_2\text{O}_2\cdot$, $\text{CCl}_3\text{O}_2\cdot$, and $\text{CBr}_3\text{O}_2\cdot$ Radicals With Alkenes in Methanolic Solutions

Compound	K, L mol ⁻¹ s ⁻¹			
	$\text{CF}_3\text{CCl}_2\text{O}_2\cdot$	$\text{CCl}_3\text{O}_2\cdot$ ^a	$\text{CBr}_3\text{O}_2\cdot$ ^a	σ^* ^b
2-buten-1-ol	4.9×10^4	2.5×10^4	2.3×10^4	1.54
3-methyl-3-buten-1-ol	9.3×10^4	5.0×10^4	5.0×10^4	1.16
3-methyl-2-buten-1-ol	3.3×10^5	1.6×10^5	1.2×10^5	1.05
cyclohexene	2.1×10^5	9.5×10^4	9.1×10^4	0.78
2-methyl-2-butene	2.8×10^6	1.3×10^6	—	0.49
1-methyl-1-cyclohexene	3.2×10^6	1.3×10^6	—	0.29
2,3-dimethyl-2-butene	3.1×10^7	1.4×10^7	1.0×10^7	0.00
2-methyl-3-ethyl-2-pentene	9.7×10^6	3.2×10^6	2.5×10^6	-0.20
1,2-dimethylcyclohexene	8.0×10^6	3.4×10^6	3.3×10^6	-0.20
styrene	5.7×10^5	3.2×10^5	2.1×10^5	2.07

^a (Alfassi, Huie, and Neta 1993) except for the results for 2-methyl-2-butene and 1-methyl-1-cyclohexene, which were measured in this study.

^b Taft σ^* substituent constants calculated as the sum of the individual σ^* values of the substituents on each double bond, taking: H = +0.49; CH₃ = -0.10; C₆H₅ = +0.60; CH₂OH = +0.56; CH₂CH₂OH = +0.18 (estimated from other values). For the cyclic alkenes, we calculated the values by assuming two open ends.

correlation observed between the logarithms of the rate constants and the Taft σ^* substituent constants. The values of σ^* , calculated as the sum of the individual values for the substituents on the double bond (Taft 1956), are included in Table 1. The correlation for the reactions of $\text{CF}_3\text{CCl}_2\text{O}_2\cdot$ with aliphatic alkenes and earlier similar correlations (Nahor and Neta 1991; Alfassi, Huie, and Neta 1993) shows considerable scatter. (Styrene, where the substituent effect may also involve resonance stabilization, is not included in the correlation.) Much better correlations are found, however, among the rate constants for the various peroxy radicals. We have determined the correlation between the rate constants for the reactions of $\text{CF}_3\text{CCl}_2\text{O}_2\cdot$ with the corresponding reactions of $\text{CCl}_3\text{O}_2\cdot$; and a similar correlation is observed with $\text{CBr}_3\text{O}_2\cdot$. The scatter in the σ^* plots points to a general tendency for the reactions of the peroxy radicals with the larger alkenes to be slower than expected. For example, the reactions of 2-methyl-3-ethyl-2-pentene and 1,2-dimethylcyclohexene are slower than the reaction of 2,3-dimethyl-2-butene, even though they have an equal degree of substitution and their σ^* values are more negative. These results indicate that there is a steric effect in the reactions of the larger alkenes with peroxy radicals.

4.2 Effect of Peroxyl Radical Substituents on the Addition Reaction. The results for a number of different haloperoxyl radical reacting with five alkenes are presented in Table 2 (included, for comparison, are some results for $\text{CF}_3\text{O}_2\cdot$, $\text{CCl}_3\text{O}_2\cdot$, and $\text{CBr}_3\text{O}_2\cdot$ from earlier work). It is clear that the trifluoromethylperoxyl radical is more reactive than the trichloromethylperoxyl radical, which is slightly more reactive than the tribromomethylperoxyl radicals. Substitution of a single chlorine or bromine for a fluorine in $\text{CF}_3\text{O}_2\cdot$ reduces the reactivity by a factor of 2. Substitution of two chlorine atoms for two fluorine atoms, as between $\text{CF}_3\text{CF}_2\text{O}_2\cdot$ and $\text{CF}_3\text{CCl}_2\text{O}_2\cdot$, leads to a reduction in reactivity of a factor of about 7. Substitution of a CF_3 group for an F atom does not have a clear effect: it doubles the rate constant for cyclohexene, but appears to be slightly deactivating for 2,3-dimethyl-2-butene and for 1,1-dimethyl cyclohexene. Substitution of two CF_3 groups leads to a result which appears even more anomalous: $\text{CF}_3\text{O}_2\cdot$ and $(\text{CF}_3)_2\text{CFO}_2\cdot$ react with cyclohexene with equal rate constants; for the more substituted alkenes, $\text{CF}_3\text{O}_2\cdot$ is the more reactive. These results seem to suggest an effect of steric hindrance, which reduces the rate constants for the reactions of $\text{CF}_3\text{CF}_2\text{O}_2\cdot$ with the larger alkenes and the rate constants for the reactions of $(\text{CF}_3)_2\text{CFO}_2\cdot$ with all the alkenes.

5. CF_3I PHOTOCHEMISTRY

Trifluoroiodomethane (CF_3I) is a leading Halon replacement candidate compound which is being considered as a drop-in replacement for Halon 1301. Unlike the situation with many of the perfluoro- (PFC), hydrofluoro- (HFC), and hydrochlorofluorocarbons (HCFC), the atmospheric chemistry of iodinated compounds is generally poorly understood. Presently, there are a number of data gaps in the photochemical behavior and reaction kinetics of iodinated compounds. One of the most important photophysical properties that affects the atmospheric lifetime, and thus the ODP and GWP, is the absorption cross section of the parent compound. This quantity is temperature dependent and, thus, has to be measured over a sufficiently wide temperature range. Figure 1 gives the result of recent measurements of the temperature dependent absorption cross section with the highest cross section curve at 340 nm corresponding to 333 K, while the lowest corresponds to 218 K. Figure 2 shows the three separate absorption bands that best fit the total absorption at the absorption peak. In addition, the quantum yield for formation of the photoproducts CF_3 and I atoms needs to be determined, since it can range between zero and one. These measurements are currently underway. Figure 3 shows the experimental setup for this work involving detection of CF_3 and CF_2 in the $1,250\text{--}1,275\text{ cm}^{-1}$ range.

Table 2. Rate Constants for Reactions of Haloalkylperoxyl Radicals With Alkenes^a in Methanolic Solutions

Radical	k, L mol ⁻¹ s ⁻¹				
	CH	MB	MCH	DMB	DMCH
CBr ₃ O ₂ ·	9.1 × 10 ^{4b}	—	—	1.0 × 10 ^{7b}	3.3 × 10 ^{6b}
CCl ₃ O ₂ ·	9.5 × 10 ^{4b}	1.3 × 10 ⁶	1.3 × 10 ⁶	1.4 × 10 ^{7b}	3.4 × 10 ^{6b}
CF ₃ O ₂ ·	7.5 × 10 ^{5b}	1.8 × 10 ⁷	1.7 × 10 ⁷	2.2 × 10 ^{8b}	7.5 × 10 ^{7b}
CF ₂ ClO ₂ ·	4.5 × 10 ⁵	9.4 × 10 ⁶	9.1 × 10 ⁶	8.3 × 10 ⁷	3.2 × 10 ⁷
CF ₂ BrO ₂ ·	4.9 × 10 ⁵	7.9 × 10 ⁶	7.7 × 10 ⁶	7.7 × 10 ⁷	2.7 × 10 ⁷
CF ₃ CCl ₂ O ₂ ·	2.1 × 10 ⁵	2.8 × 10 ⁶	3.2 × 10 ⁶	3.1 × 10 ⁷	8.0 × 10 ⁶
CF ₃ CF ₂ O ₂ ·	1.7 × 10 ⁶	1.9 × 10 ⁷	2.6 × 10 ⁷	1.3 × 10 ⁸	6.7 × 10 ⁷
(CF ₃) ₂ CFO ₂ ·	7.7 × 10 ⁵	6.8 × 10 ⁶	6.4 × 10 ⁶	5.0 × 10 ⁷	2.5 × 10 ⁷
⁻ O ₂ CCl ₂ O ₂ ·	—	—	—	<1 × 10 ^{5c}	—

^a CH - cyclohexene, MB - 2-methyl-2-butene, MCH - 1-methylcyclohexene, DMB - 2,3-dimethyl-2-butene, DMCH - 1,2-dimethylcyclohexene.

^b Alfassi, Huie, and Neta (1993).

^c Addition of 124 mmol L⁻¹ DMB to a solution containing 4.8 mmol L⁻¹ chlorpromazine resulted in no measurable change in the rate of formation of the CIPz radical, suggesting that the rate constant for the reaction of ⁻O₂CCl₂O₂· with DMB is less than 10⁵ L mol⁻¹ s⁻¹.

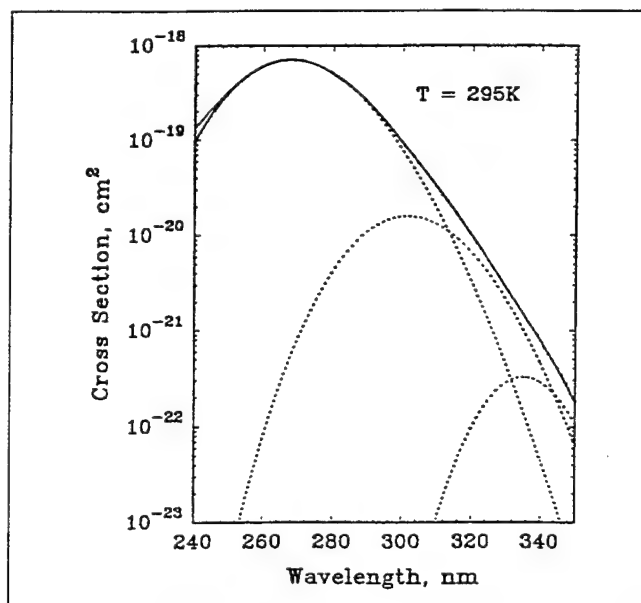


Figure 1. Curve fits for three contributing transitions in CF₃I absorption.

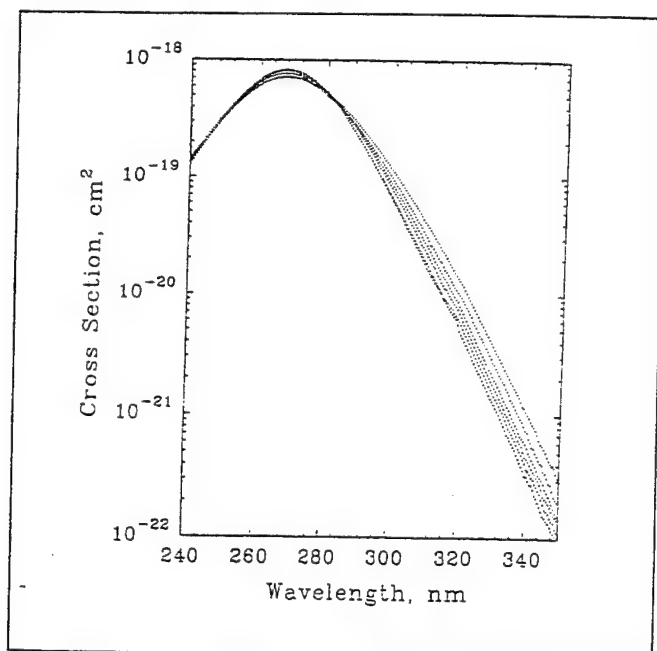


Figure 2. Temperature dependent CF₃I absorption cross sections.

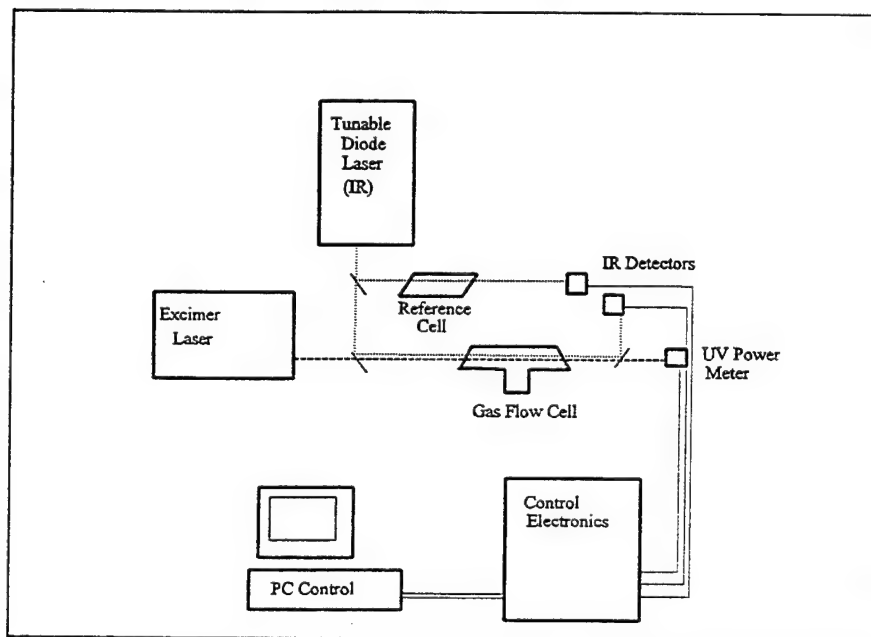


Figure 3. Schematic of the photochemistry experimental apparatus.

6. CONCLUSION

The gas-phase rate constant for the reaction of $\text{CF}_3\text{O}_2\cdot$ with NO is about $9 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$; the reaction of $\text{CF}_3\text{O}_2\cdot$ with NO_2 , at the high pressure limit, has a rate constant of about 4×10^9 (Wallington et al. 1992). In this work, we have found that the rate constants for the reactions of the halogenated peroxy radicals with alkenes in methanol reach a maximum at about $2 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$. We do not yet know the reactivity of halogenated peroxy radicals towards alkenes in the *gas phase*. The reactions of $\text{CCl}_3\text{O}_2\cdot$ with alkenes do show a variation in rate constant with solvent, but no particular correlation with solvent parameters was found (Alfassi, Huie, and Neta 1993). Rate constants for the reactions of some organic peroxy radicals derived from alcohols with nitric oxide were found to be similar in water and alcoholic solvents to those measured in the gas phase (Padmaja and Huie 1993).

The fact that the rate constants do not continue to increase with increasing fluorine substitution for the more reactive alkenes but, instead, decrease, suggests that the rate constants for the reactions of halogenated peroxy radicals with terpenes or other atmospheric alkenes will be at this value or lower. Therefore, the concentration of alkenes in the atmosphere must be at least 20–50 times greater than that of the nitrogen oxides for the reaction rates to be of equal magnitude. The concentration of nitrogen oxides are highly variable, with a global value of about 0.1–1 ppb. In urban areas, the concentration averages about 24 ppb (Graedel 1978). Alkene concentrations are also highly variable. Most measurements have been made in urban areas and range up to 20 ppb for individual branched-chain alkenes. (Ethene and propene have even higher concentrations; they are unlikely, however, to be reactive toward these peroxy radicals.) In rural areas, the concentrations of these alkenes, with the exception of isoprene, are likely to be much lower. Terpenes, however, are emitted in large quantities by vegetation. Ambient concentrations of 0.1–1 ppb have been reported near forests (Graedel 1978). Together, these data suggest that the concentrations of the nitrogen oxides and of the reactive alkenes are likely to be similar within a given area, probably within a factor of 10. This would indicate that the halogenated peroxy radicals are not likely to react with the alkenes, but will react with ambient NO and NO_2 .

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